

# Alkyl Pyrocarbonate Electrolyte Additives for Performance Enhancement of Li Ion Cells

M. C. Smart, B. V. Ratnakumar, and S. Surampudi

*Electrochemical Technologies Group  
Jet Propulsion Laboratory  
California Institute of Technology  
4800 Oak Grove Drive  
Pasadena, CA 91109*

## Abstract

Lithium ion rechargeable batteries are being developed for various aerospace applications under a NASA-DoD interagency program. Several of these applications possess many challenging performance requirements, specifically long cycle life for LEO and GEO satellites and excellent low temperature performance for the Mars Lander and Rover missions.<sup>1-3</sup> Accordingly, we have been pursuing research studies to achieve improvements in the low temperature performance, long cycle life and calendar life of lithium ion cells. The studies are mainly focused on electrolytes, to identify advanced electrolyte formulations or new electrolyte additives to enhance Li ion mobility (at low temperatures) and stability toward the electrode. The latter approach is particularly aimed at the formation of suitable SEI (solid electrolyte interphase) layers on carbonaceous anodes. In this paper, we report the beneficial effect of using alkyl pyrocarbonates as electrolyte additives to improve the low temperature performance of lithium ion cells.

## Introduction

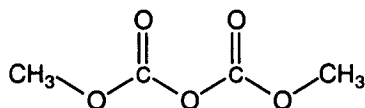
Both NASA and the Air Force have interest in lithium-ion batteries with improved low temperature performance for a number of future applications. Under sponsorship by the Mars Exploration Program and a DARPA TRP program (SAFT America, Inc.) we have focused upon developing advanced electrolyte systems with improved tolerance to extreme temperatures. Earlier work has led to the identification of a carbonate-based electrolyte, consisting of 1.0 M  $\text{LiPF}_6$  in EC + DEC + DMC (33:33:34), that has been shown to have excellent performance at  $-20^\circ\text{C}$ .<sup>4,5</sup> However, many applications, including future Mars Rovers, might be required to operate at temperatures as low as  $-40^\circ\text{C}$  and high discharge rates (C/2). In addition, improvements of charge acceptance at low temperature is also desirable, especially in light of the fact that the charge process (carbon lithiation) is generally much less facile than the corresponding discharge process (carbon de-lithiation).

In previous work, it was shown that the nature of the electrode films can influence the low temperature performance of lithium ion cells probably more

significantly than the conductivity of the electrolyte. Thus, although an electrolyte may possess high conductivity over a range of temperatures (a necessary but not sufficient condition) the resistance of the resultant surface film which form on the electrode surface may dominate and inhibit lithium intercalation/de-intercalation kinetics. It is therefore essential to optimize an electrolyte (solvents and salt types) in terms of both conductivity and SEI formation characteristics. Alternatively, one can design highly conductive formulations to which electrolyte additives are incorporated which facilitate the formation of an SEI of desirable properties. An example of this approach involves the addition of  $\text{CO}_2$  to electrolyte formulations with the prospect of forming  $\text{Li}_2\text{CO}_3$ , which possesses high ionic conductivity, on the surface of lithium or carbonaceous anodes.<sup>6</sup> Most of these studies, however, have been carried out with the intent of improving the cycle life characteristics and little focus has been devoted in these approaches to improving the low temperature performance of lithium ion cells. We have undertaken an investigation into the effect of pyrocarbonate-based solvent as electrolyte additives to enhance the low temperature performance by means of producing a stable, resilient SEI layer with improved lithium intercalation/de-intercalation kinetics.

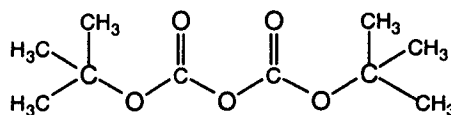
The use of pyrocarbonate additives to the electrolyte has been mentioned briefly in the literature. These additives were recognized for their potential to generate  $\text{CO}_2$  in-situ, via decomposition, which would aid in the formation of suitable SEI on graphite. Researchers from Sony<sup>7</sup> reported the use of pyrocarbonates in non-aqueous liquid electrolyte secondary cells. The group describes the use of pyrocarbonates having the formula  $(\text{ROCO})_2\text{O}$ , wherein R is an alkyl group selected from the group consisting of  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$  and  $\text{C}_3\text{H}_7$ . Researchers at SRI have reported the use of di-*t*-butyl pyrocarbonate in multi-component electrolyte formulations with non-flammable characteristics. The benefit of the pyrocarbonate additives was rationalized for its flame retardant,  $\text{CO}_2$  generating properties.<sup>8</sup> Coowar and coworkers have demonstrated that addition of dimethyl pyrocarbonate to binary electrolyte mixtures (i.e., EC+DMC) results in smaller irreversible capacity losses and lower capacity fade.<sup>9</sup>

Our recent studies on the low temperature electrolytes have led to several electrolyte formulations, i.e., the ternary, equi-proportion mixture of EC, DMC and DEC, described previously and quaternary solvent mixtures using aliphatic esters and asymmetric alkyl carbonates, such as ethyl methyl carbonate, as quaternary components to the EC:DEC:DMC solvent mixtures.<sup>10</sup> We report here the beneficial effects of alkyl pyrocarbonate additives to some of these solvent mixtures on the (low temperature) performance and stability of lithium ion cells. We have studied the effects of two pyrocarbonate additives, i.e., dimethyl pyrocarbonate, **1**, and dibutyl pyrocarbonate, **2**, in varying amounts (5 and 25 vol%).



Dimethyl pyrocarbonate

**1**



Di-*t*-butyl pyrocarbonate

**2**

## Experimental

Since the intent of these studies is to assess the characteristics of the SEI films formed, such as the ionic resistance, ease of charge transfer across the interface especially at low temperatures, and the stability of the film during storage, we fabricated Li-carbon (MCMB) half-cells with electrolytes varying in the pyrocarbonate type, and solvent composition. The electrolytes chosen for these studies include:

- (1) 1.00 M  $\text{LiPF}_6$  EC+DEC+DMC (1:1:1)
- (2) 0.75 M  $\text{LiPF}_6$  EC+DEC+DMC+ DMPC (1:1:1:1)
- (3) 0.95 M  $\text{LiPF}_6$  5% DMPC in the baseline (1)
- (4) 0.95 M  $\text{LiPF}_6$  5% DBPC in the baseline (1)
- (5) 0.75 M EC+DEC+DMC+EA+DBPC (5:5:5:4:1)

The ethylene carbonate-based electrolyte solutions used in this study were obtained from Mitsubishi Chemical, with the desired concentration of the electrolyte salt contained within. The pyrocarbonate-based solvents (dimethyl pyrocarbonate and di-*t*-butyl pyrocarbonate) were obtained from Aldrich Chem. Co. and used as received.

The electrolyte formulations were investigated in lithium-MCMB carbon half-cells, equipped with lithium reference electrode, to determine their compatibility with graphite electrodes. In addition to half-cells, experimental cells were constructed with MCMB and  $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$  electrodes equipped with reference electrodes to examine the compatibility of these materials in full cells where one can monitor the potential of both electrodes during operation, especially at low temperatures. In addition to studying the charge/discharge characteristics of these cells at various temperatures, a.c. impedance and D.C. micropolarization techniques have been employed to probe the nature of the passive film.

## Results and Discussion

### Lithium-MCMB Half-Cell Studies

A number of lithium-graphite cells were fabricated to study the viability of using these potential low temperature electrolytes. The use of these three electrode half-cells enables us to study the effect of different electrolytes upon the film formation characteristics on carbon electrodes (MCMB-based materials), as described below.

### Charge/discharge characteristics

One aspect of studying the charge/discharge characteristics of the lithium metal-carbon half-cells included the assessment of the observed irreversible and reversible capacities as a function of electrolyte type. In Fig. 1, the reversible capacities delivered after the fifth formation cycle of the cells are shown, with most of the pyrocarbonate containing electrolytes resulting in higher reversible capacity compared to the baseline. The results of the initial cycling in terms of the reversible and irreversible capacities are summarized in Table 1. From the data, it is apparent that using a pyrocarbonate-based solvent in large proportion (treated as a co-solvent, rather than an electrolyte additive) results in lower reversible capacities. In addition, it is apparent that the use of pyrocarbonate additives in lower concentrations (i.e., 5% or less) is beneficial in terms of

the high reversible capacity (>310 mAh/g) when compared to the baseline electrolyte. The somewhat low reversible capacities observed with the carbon electrodes can be attributed to the fact that (a) the electrodes were charged to only 0.010 V vs. Li<sup>+</sup> to prevent the possibility of lithium plating, and due to (b) the expected loss in capacity associated with the formation of the SEI layer during the conditioning cycles.

Electrolyte Type	Charge Capacity (Ahr) 1st Cycle	(mAh/g)	Discharge Capacity (Ahr) 1st Cycle	(mAh/g)	Charge Capacity (Ahr) 5th Cycle	(mAh/g)	Discharge Capacity (Ahr) 5th Cycle	(mAh/g)	Efficiency (Coulombic)
1.0 M LUPF6 EC+DEC+DMC (1:1:1)	0.62899	0.33999	0.57811	0.31249	0.60057	0.32464	0.58433	0.31585	0.91910
0.95 M LUPF6 EC+DEC+DMC+DMPC (31.67:31.67:31.67:5)	0.67313	0.36385	0.61758	0.33383	0.63755	0.34462	0.62308	0.33680	0.91748
0.95 M LUPF6 EC+DEC+DMC+DBPC (31.67:31.67:31.67:5)	0.67123	0.36283	0.60087	0.32479	0.61615	0.33305	0.61152	0.33055	0.89518
0.75 M LUPF6 EC+DMC+DEC+EA+DBPC (5:5:5:4:1)	0.65838	0.35588	0.59393	0.32104	0.62153	0.33596	0.61956	0.33489	0.90212
0.75 M LUPF6 EC+DEC+DMC+DMPC (1:1:1:1)	0.59588	0.32210	0.54757	0.29598	0.56402	0.30488	0.54821	0.29633	0.91894
1.0 M LUPF6 EC+DEC+EMC (1:3:1)	0.62716	0.33901	0.57813	0.31250	0.55848	0.30188	0.54910	0.29681	0.92182

Table. 1. Tabulation of the reversible and irreversible capacities of MCMB electrodes (Li-C cells) in contact with various electrolytes.

Since the major objective of this study was to determine the beneficial properties of pyrocarbonate-based additives upon the low temperature performance of lithium ion cells, the cells were charged and discharged at low temperatures (-20°C and -40°C) in addition to being characterized by a number of electrochemical techniques. Fig. 2 shows the lithium de-lithiation capacities for a number of Li-MCMB cells with different electrolytes at -20°C at a modest rate (25mA or ~ C/12). When the carbon electrodes are fully lithiated at room temperature and de-lithiated at low temperature all of the samples are somewhat comparable, with slightly higher capacity (85-90% of the room temperature capacity) observed for the cells containing 5% of the pyrocarbonate additive. However, the electrode polarization displayed for some of the cells containing the pyrocarbonate additives was significantly reduced in some cases, exceeding 200 mV improvement.

Following the first carbon de-lithiation at low temperature, the Li-MCMB cells were discharged at -20°C (carbon lithiation process) to 0.010 V. In general, it has been observed that the kinetics of the lithiation of carbon is less facile than that of the de-intercalation process and limits the performance of the cells under conditions of continuous cycling at low temperature. As shown in Fig. 3, the lithium intercalation capacities of the MCMB electrodes at -20°C are much lower than the corresponding de-intercalation process. Also significant is the fact that there is more variance in the cell performance depending upon the electrolyte type, implying that the nature of the SEI is impacting the corresponding lithium intercalation kinetics at low temperature. Of the cells investigated, the electrodes in contact with electrolytes containing di-*t*-butyl

pyrocarbonate displayed 3-4 times greater intercalation capacity. This is presumably due to the fact that the additive helped to produce an electrode film with improved lithium kinetics resulting in low electrode polarization. When the cells were charged a second time at  $-20^{\circ}\text{C}$  (second lithium de-intercalation of carbon), as shown in Fig.4, the cells containing DBPC additives dramatically outperformed the baseline cell.

### **AC Impedance Measurements**

In addition to studying the charge/discharge characteristics of these cells, a.c. impedance was used to probe the nature of the anode passivating film. Measurements were conducted for each cell after the formation process (5 cycles), as well as, after the cells had been subjected to cycling and characterized in terms of the self-discharge behavior. AC impedance measurements were also taken at a number of temperatures (25, 0, and  $-20^{\circ}\text{C}$ ) to determine the impact of temperature upon the film resistance of the samples. It was generally observed that the film resistance dramatically increased upon going to lower temperatures. These results suggest that the nature of the SEI layer on the carbon electrode plays a large role in determining the low temperature discharge performance in addition to the bulk resistivity of the electrolyte. When the cells containing the pyrocarbonate-based electrolytes were compared with all-carbonate-based baseline systems after the formation cycles at room temperature, as shown in Fig.5, it was evident that the pyrocarbonate-based systems resulted in lower film resistances of the MCMB electrodes.

With the pyrocarbonate containing cells, a dramatically lower film resistance was observed as compared to the standard carbonate-based mixtures. This trend was apparent at all temperatures, being especially dramatic at  $-20^{\circ}\text{C}$  and lower. As illustrated in Fig. 6. and Fig. 7, nearly an eight-fold decrease in the film resistance was observed with the pyrocarbonate-containing electrolyte compared to the baseline ternary solution. This can be mainly attributed to the desirable SEI film properties, which were formed in the presence of carbon dioxide, or other pyrocarbonate decomposition by-product. This implies that the addition of pyrocarbonate additives (co-solvents) can serve as a technique to produce more desirable surface films on carbon electrodes, which possess low film and charge transfer resistances, resulting in more facile lithium kinetics. The data also suggests that the use of pyrocarbonates can be extended to other potential low temperature electrolyte formulations with the expectation of improved SEI formation. It was envisioned that the pyrocarbonate additives would enable the effective use of solvents such as methyl acetate, ethyl acetate, and methyl formate, which have been observed to result in electrodes with large interfacial resistance values.

### **Linear Polarization Measurements**

DC micropolarization techniques were also employed to study the charge transfer behavior of the passivating films on the MCMB electrodes at various temperatures. The polarization resistances of the electrodes were calculated from the slope of the linear plots generated under potentiodynamic conditions at scan rates of  $0.02\text{ mV/s}$ . As shown in Fig. 8 and Fig. 9, the polarization resistance was consistently lower for the cells possessing pyrocarbonate-containing electrolytes compared to the all-carbonate-based systems, being especially dramatic at low temperatures. Of the pyrocarbonates

studied, the di-*t*-butyl pyrocarbonate-based systems yielded the lowest polarization values, correlating well with the charge-discharge characteristics previously mentioned. As shown in Fig.10, the cell containing the 0.75 M LiPF<sub>6</sub> EC+DEC+DMC+EA+DBPC (5:5:5:4:1) resulted in a polarization resistance value (1.4 kOhm) approximately eight times lower than that of the baseline electrolyte 1.00 M LiPF<sub>6</sub> EC+DEC+DMC (1:1:1) (10.1 kOhm) at -20°C.

### **Tafel Polarization Measurements**

The limiting current densities were also determined for the lithium de-intercalation process from the graphite electrodes by conducting Tafel polarization measurements to evaluate the rate capability of the electrodes in contact with the various electrolytes. These measurements were conducted on the lithium-graphite cells at various temperatures (25, 0, and -20°C), as shown in Fig. 11 and Fig. 12. When the cells were evaluated at -20°C, the electrolyte containing the di-*t*-butyl pyrocarbonate additive resulted in the least amount of electrode polarization and the highest limiting current densities implying facile lithium intercalation/de-intercalation kinetics. These results are consistent with the trends observed when the cells were evaluated using linear polarization techniques, as well as, the cell charge/discharge characteristics at low temperature.

### **Lithium-MCMB Half-Cell Studies**

In addition to evaluating pyrocarbonate-based additives in half-cells, some studies were conducted with MCMB-LiNi<sub>1-x</sub>Co<sub>x</sub>O<sub>2</sub> three electrode cells. One objective of this study was to determine if the compounds were sufficiently compatible with high voltage cathodes, such as LiNi<sub>1-x</sub>Co<sub>x</sub>O<sub>2</sub>, and if the beneficial passivating properties would manifest themselves at the full cell level. As shown in Fig. 13 and Fig 14, the normal characteristics expected during the initial formation cycles are displayed with good reversibility. One advantage of investigating potential electrolytes in these types of full-cells is that one can monitor individual electrode potentials during operation and determine the extent of polarization displayed by each respective electrode. For example, the charge behavior at low temperature (-20°C) has been studied for different cells, including one containing the baseline electrolyte formulation (Fig. 15) and one containing a pyrocarbonate-based electrolyte (Fig. 16). As illustrated, the potential of the anode in the baseline cell under conditions of high rate charge is negative and suggests that lithium plating is occurring under these conditions. However, in the case of the pyrocarbonate containing cell the anode potential is never polarized to negative values, implying that lithium plating under similar conditions is less likely to occur.

### **Conclusions**

Additions of pyrocarbonates (e.g., dimethyl or preferably di-*t*-butyl) to electrolyte solutions of lithium ion batteries have been demonstrated to result in improved performance, especially at low temperature. The beneficial effect upon the performance of Li-ion cells is believed to be due to the formation of desirable surface films, composed of Li<sub>2</sub>CO<sub>3</sub> presumably. In addition to improved charge/discharge properties at low temperatures, enhanced Li ion intercalation/de-intercalation kinetics have been observed from electrochemical measurements.

## Acknowledgment

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, for the Mars Exploration Program and a DARPA TRP program under contract with the National Aeronautics and Space Administration (NASA).

## References

1. M. C. Smart, B. V. Ratnakumar, L. Whitcanack, J. Byers, S. Surampudi, and R. Marsh, "Performance Characteristics of Lithium-Ion Cells for NASA's Mars 2001 Lander Applications", Proceedings of the Intersociety Energy Conversion Engineering Conference (IECEC), Vancouver, British Columbia, Aug., 1999.
2. B. V. Ratnakumar, M. C. Smart, R. Ewell, S. Surampudi, and R. Marsh, "Performance Characteristics of Lithium-Ion Cells for Mars Sample Return Athena Rover", Proceedings of the Intersociety Energy Conversion Engineering Conference (IECEC), Vancouver, British Columbia, Aug., 1999.
3. M.C. Smart, B.V. Ratnakumar, C.-K. Huang, and S. Surampudi, *SAE Aerospace Power Systems Conference Proceedings*, P-322, p. 7-14 (1998).
4. M.C. Smart, C.-K. Huang, B.V. Ratnakumar, and S. Surampudi, "Development of Advanced Lithium-Ion Cells with Improved Low Temperature Performance", Proceedings of the Intersociety Energy Conversion Engineering Conference (IECEC), Honolulu, Hawaii, July, 1997.
5. M.C. Smart, B.V. Ratnakumar, and S. Surampudi, "Electrolytes for Low Temperature Lithium-Ion Batteries Based on Mixtures of Aliphatic Carbonates", *J. Electrochem.Soc.*, 1998,.
6. H. Gan and E.S. Takeuchi, *J. Power Sources*, **62**, 45 (1996).
7. N. Sugeno, U.S. Patent 5,427,874 (June 27, 1995).
8. S. Narang, S. C. Ventura, B. J. Dougherty, M. Zhao., S. Smedley, and G. Koolpe, U.S. Patent 5,830,600 (Nov. 3, 1998)
9. F. Coowar, A. M. Christie, P. G. Bruce, and C. A. Vincent, *J. Power Sources*, **75**, 144 (1998).
10. M.C. Smart, B.V. Ratnakumar, and S. Surampudi, "Development of High Conductivity Lithium-Ion Electrolytes for Low Temperature Cell Applications" Proceedings of the 38th Power Sources Conference, June, 1998.

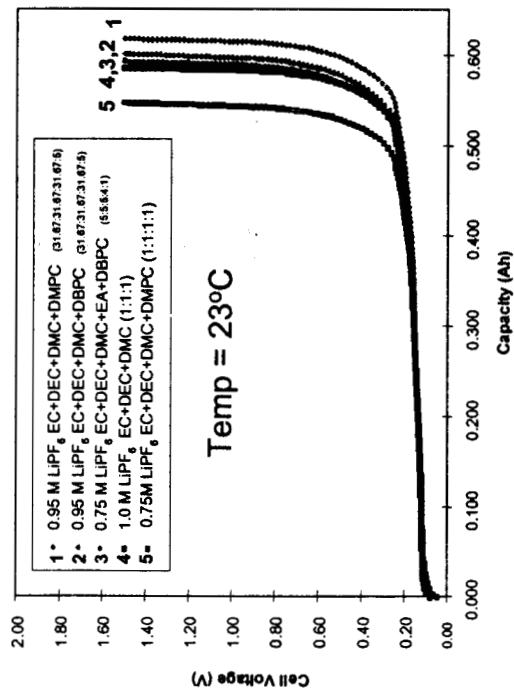


Fig. 1. Reversible capacities of lithium-MCMB cells containing different electrolytes after five formation cycles.

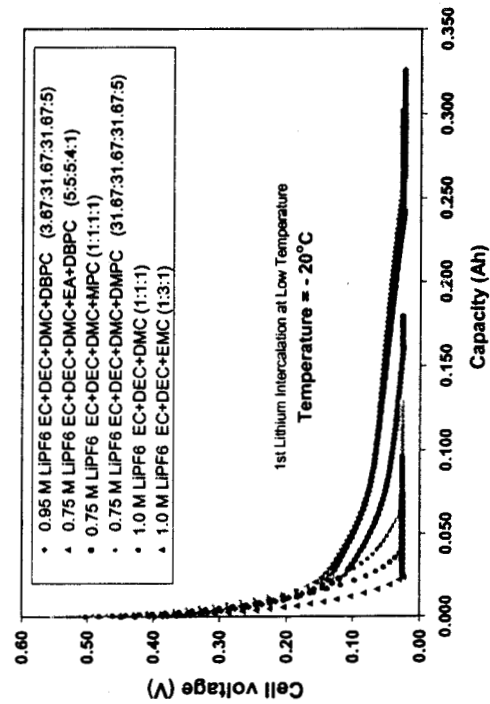


Fig. 3. First lithium intercalation step at low temperature (-20°C). Cells were discharged at constant current (25 mA) to 0.010 V.

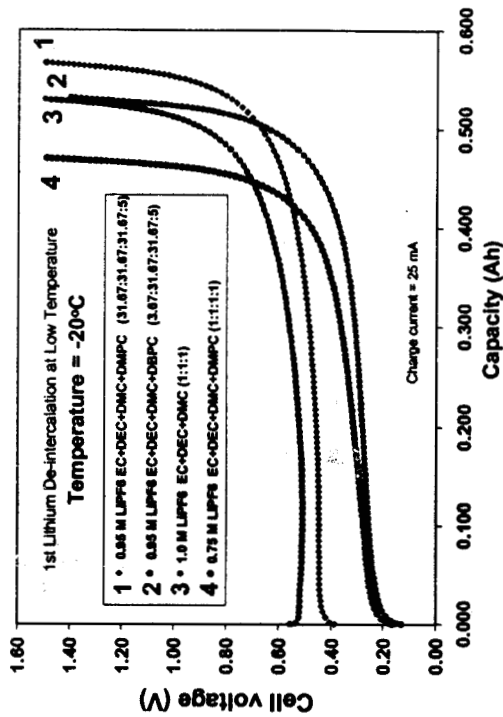


Fig. 2. Lithium de-intercalation capacities of MCMB electrodes at -20°C with the electrodes lithiated at room temperature.

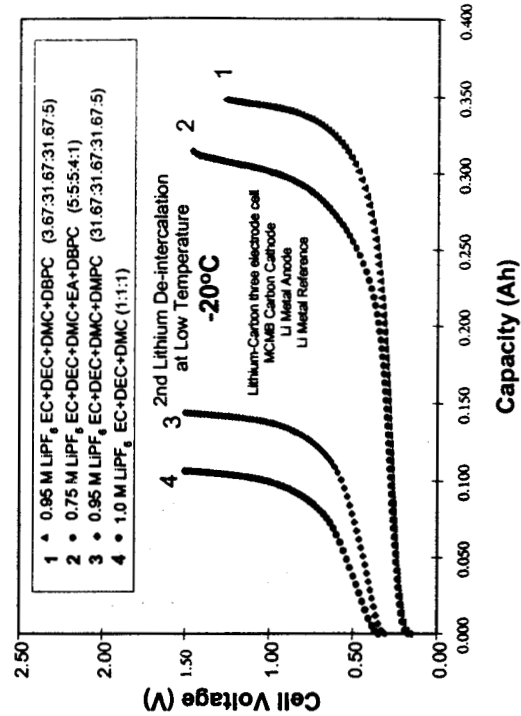


Fig. 4. Second lithium de-intercalation cycle of MCMB electrodes at -20°C. Electrodes were lithiated at -20°C prior to delithiation.



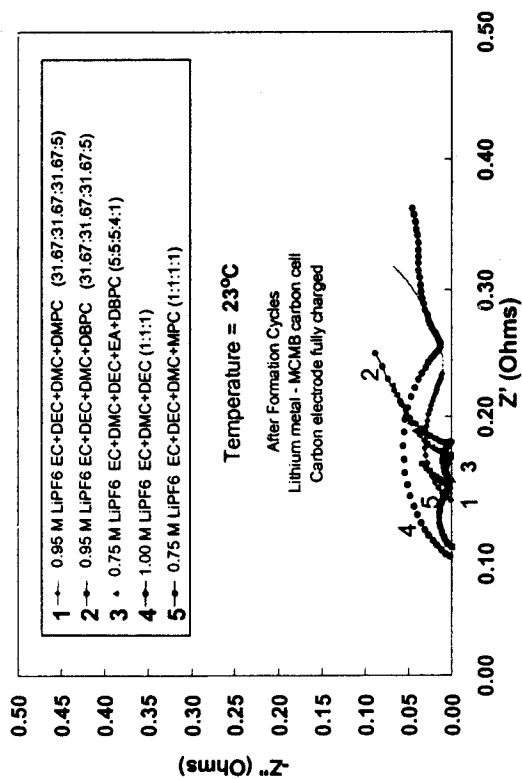


Fig. 5. EIS of MCMB electrodes at room temperature after formation cycles. Electrodes were in a full state-of-charge.

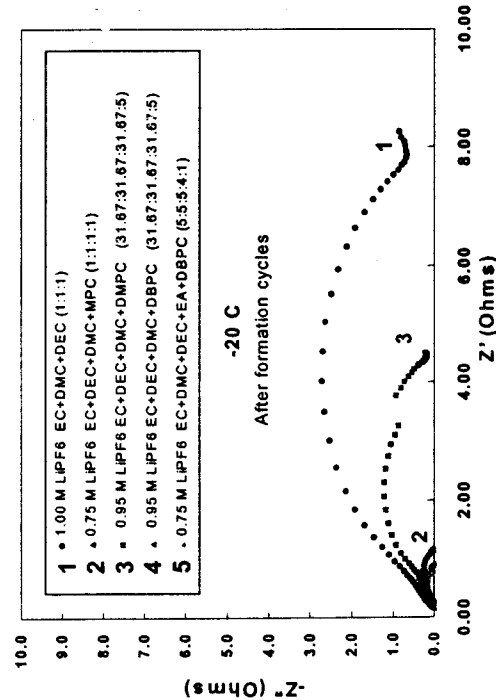


Fig. 7. EIS of MCMB electrodes at -20°C after formation cycles. Electrodes were in a full state-of-charge.

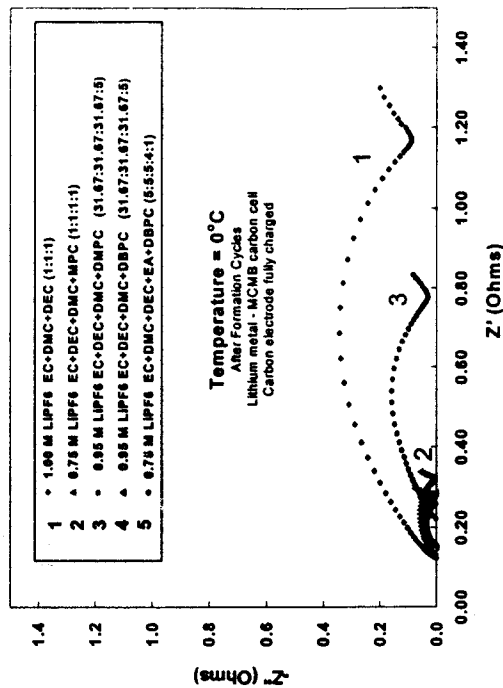


Fig. 6. EIS of MCMB electrodes at 0°C after formation cycles. Electrodes were in a full state-of-charge.

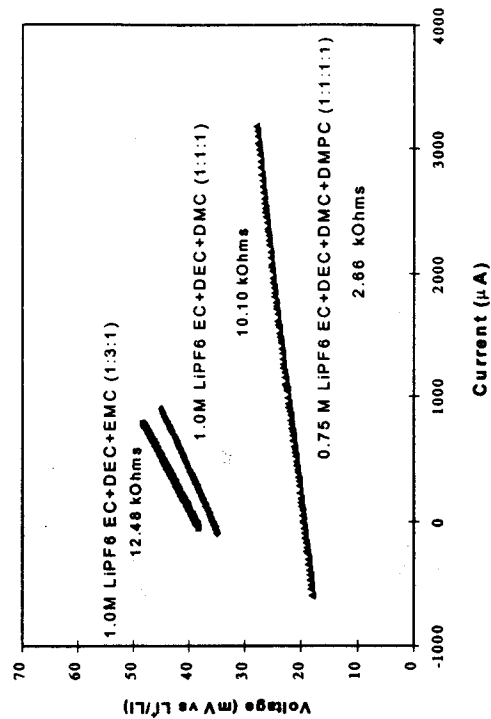


Fig. 8. DC micropolarization plots at -20°C of MCMB electrodes in contact with different electrolytes.

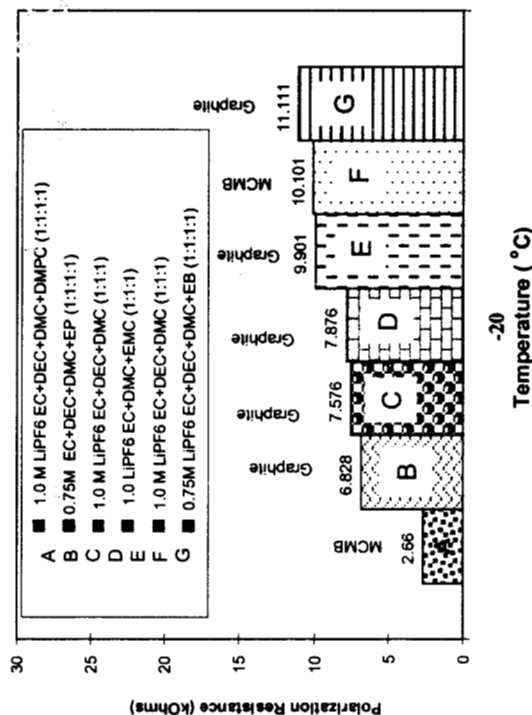


Fig. 9. Polarization resistance from DC micropolarization at -20°C of MCMB electrodes in contact with different electrolytes.

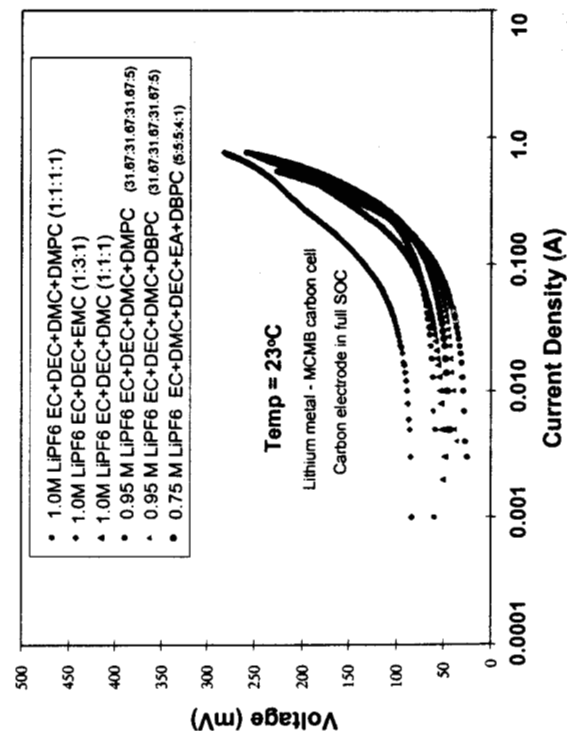


Fig. 11. Tafel polarization measurements of MCMB electrodes in contact with different electrolytes at room temperature.

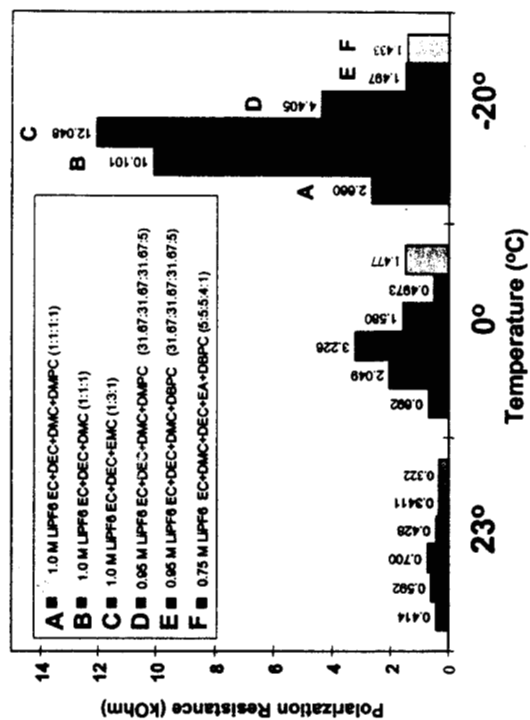


Fig. 10. Polarization resistance values of MCMB electrodes calculated from DC micropolarization measurements at different temperatures.

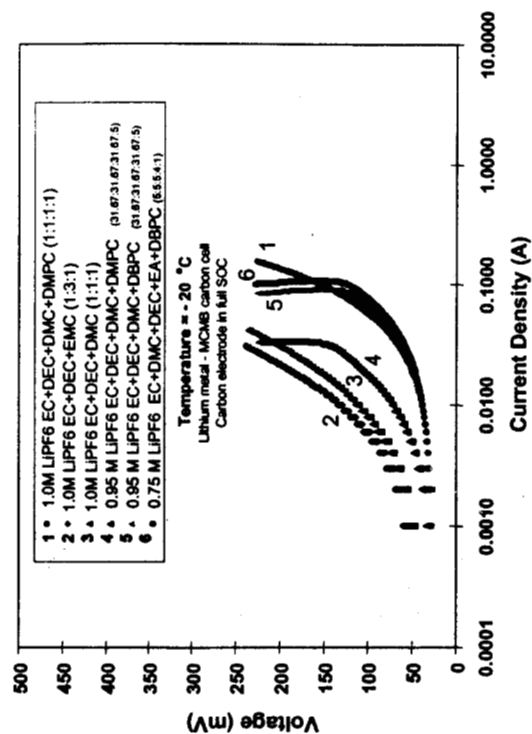


Fig. 12. Tafel polarization measurements of MCMB electrodes in contact with different electrolytes at -20°C.

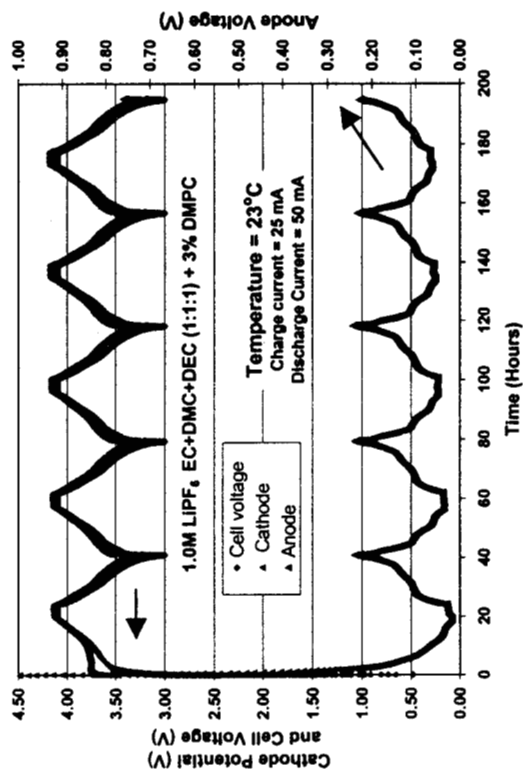


Fig. 13. First five formation cycles of a MCMB-LiCoNiO<sub>2</sub> cell with an electrolyte possessing dimethyl pyrocarbonate as an additive.

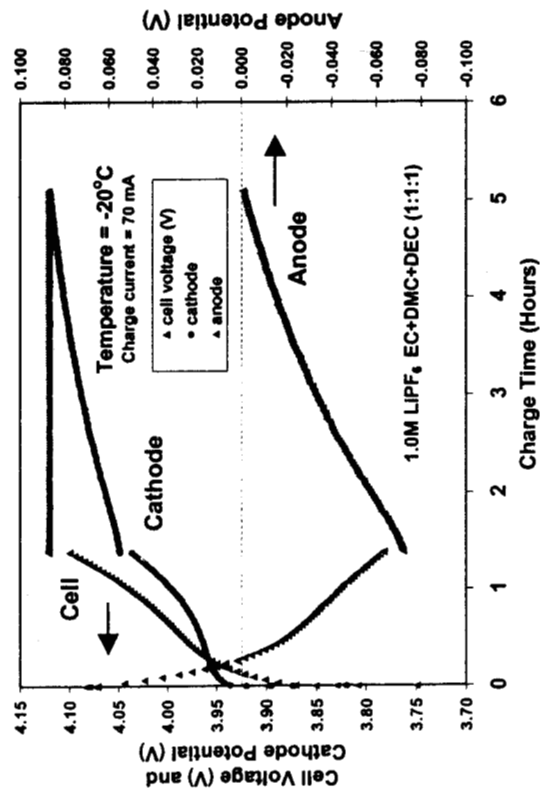


Fig. 15. Charging process of a MCMB-LiCoNiO<sub>2</sub> three-electrode cell at -20°C containing the baseline electrolyte (1.0M LiPF<sub>6</sub> in EC+DEC+DMC (1:1:1)).

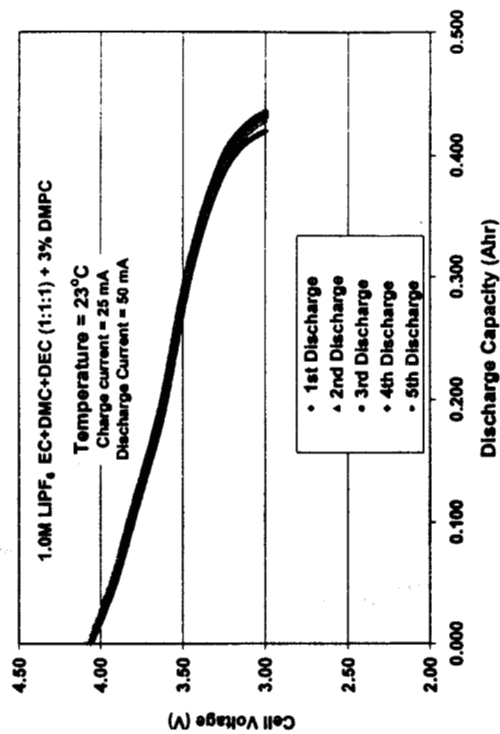


Fig. 14. First five discharges of a MCMB-LiCoNiO<sub>2</sub> cell containing the electrolyte LiPF<sub>6</sub> in EC+DEC+DMC+DMPC (1:1:1) + 3% DMPC.

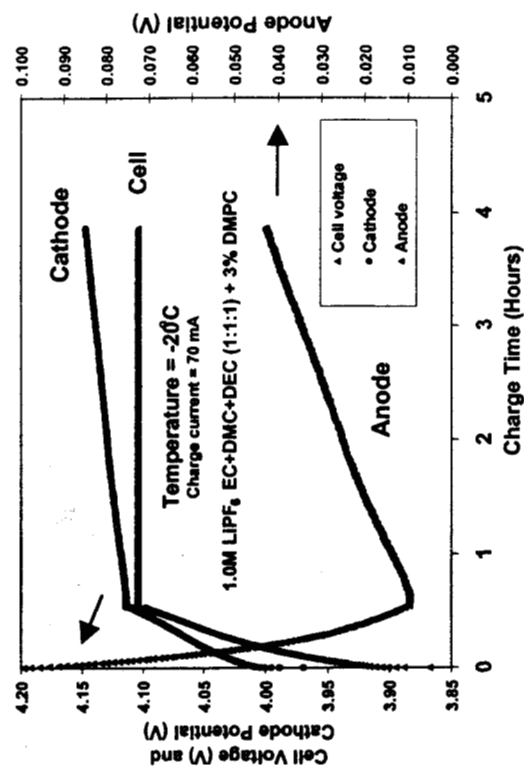


Fig. 16. Charging process of a MCMB-LiCoNiO<sub>2</sub> three-electrode cell at -20°C with a pyrocarbonate-containing electrolyte.